

## Synthesis of hollow square macrocycle as nanochannels and hollow square helices

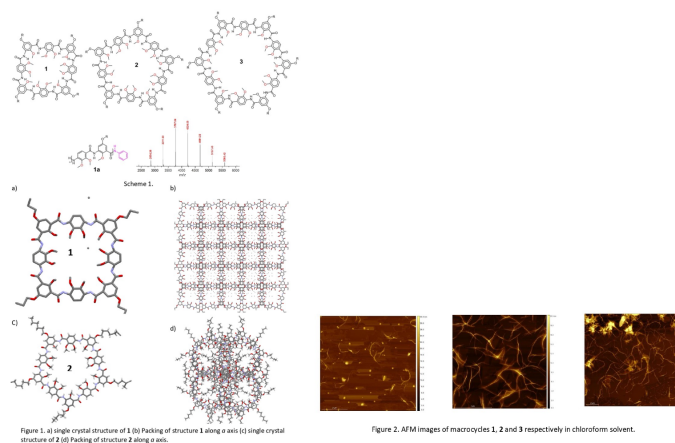
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Macrocycles and foldamers with substantial tubular cavities are intriguing and have captured significant attention. Foldamers and macrocycles with non-collapsible hydrophilic cavities have demonstrated exceptional properties in areas such as cation recognition and highly conducting membranes.<sup>1</sup> Conversely, helical foldamers and macrocycles that are rich in hydrophobic interior surfaces have shown exceptional performance in the field of water permeation.<sup>2</sup> Recent work by Takuzo Aida's group<sup>3</sup> has highlighted how these hydrophobic interior surfaces in macrocycles act as artificial water channels responsible for water permeation, using a densely fluorinated interior surface system. However, the yield of these macrocycles is low, 0.0055-0.16%, which limits their potential for use in membrane technology for water purification. Furthermore, the diacid and diamine monomers used in this system restrict the ability to synthesize helices of a specific length with narrow dispersity.

We have developed a novel category of hollow square macrocycles (1) with an internal diameter of 0.9 nm, as well as helices (1a) (Scheme 1) that feature a non-collapsible cavity of roughly 0.9 nm, and possess hydrophobic interior surfaces. Additionally, we obtained macrocycles with a diameter of 1.5 nm (2) and 2 nm (3) (Scheme 1). The square shape of the macrocycle (1) was confirmed by the solid-state structure (Figure 1a). Dynamic light scattering (DLS) of these macrocycles and helices revealed significant aggregation in chloroform solution, which increased with increasing concentration. Evidence of nanochannels was found in these macrocycles, based on the crystal structure packing of 1 and 2 (Figure 1). Furthermore, the linear stacking of macrocycles 1, 2, and 3 was confirmed by atomic force microscopy (AFM) analysis (Figure 2)

The water permeability and salt rejection tests of macrocycles and polymers, both in vesicles as well as in fabricating the membranes using interfacial polymerization, are under investigation.



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